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Application Number	10/781,389
Filing Date	February 18, 2004
First Named Inventor	Eric Davidson
Art Unit	1712
Examiner Name	TUCKER, PHILIP C.
Attorney Docket Number	HALB:001D1

ENCLOSURES (Check all that apply)

<input type="checkbox"/> Fee Transmittal Form <input type="checkbox"/> Fee Attached <input type="checkbox"/> Amendment/Reply <input type="checkbox"/> After Final <input type="checkbox"/> Affidavits/declaration(s) <input type="checkbox"/> Extension of Time Request <input type="checkbox"/> Express Abandonment Request <input type="checkbox"/> Information Disclosure Statement <input checked="" type="checkbox"/> Certified Copy of Priority Document(s) <input type="checkbox"/> Reply to Missing Parts/ Incomplete Application <input type="checkbox"/> Reply to Missing Parts under 37 CFR 1.52 or 1.53	<input type="checkbox"/> Drawing(s) <input type="checkbox"/> Licensing-related Papers <input type="checkbox"/> Petition <input type="checkbox"/> Petition to Convert to a Provisional Application <input type="checkbox"/> Power of Attorney, Revocation Change of Correspondence Address <input type="checkbox"/> Terminal Disclaimer <input type="checkbox"/> Request for Refund <input type="checkbox"/> CD, Number of CD(s) _____ <input type="checkbox"/> Landscape Table on CD	<input type="checkbox"/> After Allowance Communication to TC <input type="checkbox"/> Appeal Communication to Board of Appeals and Interferences <input type="checkbox"/> Appeal Communication to TC (Appeal Notice, Brief, Reply Brief) <input type="checkbox"/> Proprietary Information <input type="checkbox"/> Status Letter <input checked="" type="checkbox"/> Other Enclosure(s) (please identify below): Transmittal Letter w/cert. of express mailing Return Receipt Postcard
<input type="checkbox"/> Remarks		

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

Firm Name	Karen B. Tripp, Attorney at Law		
Signature			
Printed name	Karen B. Tripp		
Date	May 30, 2005	Reg. No.	30,452

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In re Application of:

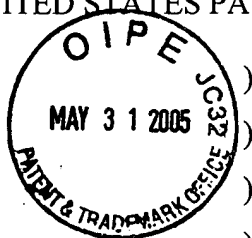
Eric Davidson

Serial No.: 10/781,389

Filed: February 18, 2004

For: Method and Composition for

Scavenging Sulphide in Drilling Fluids)



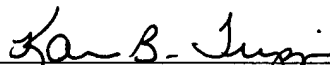
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Art Unit: 1712

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PRIORITY DOCUMENT UNDER 35 U.S.C. § 119

Dear Sir:

In the non-final Office Action mailed September 27, 2004, the Examiner acknowledged that a claim for foreign priority under 35 U.S.C. § 119 had been made but he noted that a certified copy of the priority document had not been received. That priority document was a patent application originally filed under the Patent Cooperation Treaty designating the United States among other countries.

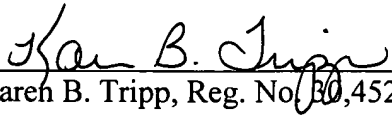
Undersigned believes that a certified copy of the priority document was provided in the United States parent application from which this application before the Examiner was divided pursuant to a restriction requirement. However, the undersigned ordered another certified copy of the priority document in response to the Examiner's statement and has now received it. That priority document is enclosed herewith.

No fee is believed due but in the event the Commissioner determines a fee to be due, the Commissioner is authorized to charge the fee for same to the undersigned's deposit account no. 50-0807.

U.S. Serial No. 10/781,389 (Attorney Dkt: HALB:001D1)
Art Unit: 1712; Examiner TUCKER, PHILIP C.

Respectfully submitted,

Date: May 30, 2005


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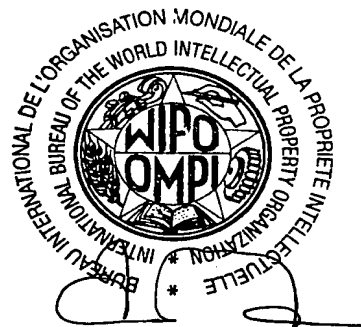
International Application No. } PCT/IB 99 / 0 1 3 4 1' International Filing Date } 29 JULY 1999
Demande internationale n° } Date du dépôt international } (29. 07. 99)

Geneva/Genève, 03 MAY 2005
(03. 05. 05)

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Head, PCT Receiving Office Section
Chef de la section "office récepteur du PCT"

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REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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International Application No.

29 JULY 1999

(29. 07. 99)

International Filing Date

INTERNATIONAL BUREAU OF WIPO
PCT International Application
Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) HALB:001

Box No. I TITLE OF INVENTION

Method and Composition for Scavenging Sulphide in Drilling Fluids

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

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State (that is, country) of nationality:
U.S.

State (that is, country) of residence:
U.S.

This person is applicant for the purposes of: ☒ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

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Aberdeen
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GB

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:
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State (that is, country) of residence:
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☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☒ agent ☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

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☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

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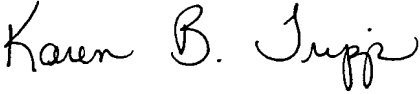
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Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
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<input type="checkbox"/> The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): _____ <small>* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.</small>				
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Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):		Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority): Date (day/month/year) Number Country (or regional Office)		
ISA/EP				
Box No. VIII CHECK LIST: LANGUAGE OF FILING				
This international application contains the following number of sheets: request : 3 description (excluding sequence listing part) : 16 claims : 2 abstract : 1 drawings : 0 sequence listing part of description : 0 Total number of sheets : 22		This international application is accompanied by the item(s) marked below: 1. <input checked="" type="checkbox"/> fee calculation sheet 2. <input checked="" type="checkbox"/> separate signed power of attorney 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: 4. <input type="checkbox"/> statement explaining lack of signature 5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 6. <input type="checkbox"/> translation of international application into (language): 7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material 8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9. <input type="checkbox"/> other (specify):		
Figure of the drawings which should accompany the abstract: Not applicable		Language of filing of the international application: English		
Box No. IX SIGNATURE OF APPLICANT OR AGENT				
Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request). <div style="text-align: center; font-size: 1.5em; margin-top: 10px;">  </div> <div style="text-align: center; margin-top: 5px;"> Karen B. Tripp, Attorney at Law </div>				

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METHOD AND COMPOSITION FOR SCAVENGING SULPHIDE IN DRILLING FLUIDS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to methods and compositions for removal or inactivation of hydrogen sulphide or soluble sulphide ions from drilling fluids used in drilling wells in subterranean formations. The invention is also applicable to removal of hydrogen sulfide or soluble sulfide ions from other fluids such as fluids in sewage systems and fluids produced from subterranean wells. The advantages of the invention are particularly appreciated with high pH fluids containing polymers.

2. Description of Relevant Art

Drilling a well in a hydrocarbon bearing subterranean formation for the production of hydrocarbons from said formation typically involves use of a drilling apparatus and drilling fluid. The drilling apparatus usually comprises a bit mounted on a string of hollow steel pipe. This hollow pipe is often used to rotate the bit to enable the bit to cut into the formation. The hollow pipe also acts as a conduit for the drilling fluid to be pumped down to the bottom of the hole, from where it rises to the surface via the annulus between the drill string and the borehole wall. The drilling fluid has many functions, one of the most important of which is to convey the cuttings from the bit downhole up to the surface of the well.

Good shear thinning rheology is an important property for drilling fluids. This property is generally achieved in one of two ways by using a dispersion of colloidal clay minerals such as smectite clays, e.g., bentonite, or by using polymers such as xanthan gum or scleroglucan that can be dispersed in aqueous solutions to give shear thinning fluids. Each approach has known advantages and disadvantages, although use of polymers seems to be the modern trend. Systems based on dispersed colloids are susceptible to the effects of dispersing and flocculating agents, whereas the rheology of polymer based fluids is more easily controlled. A disadvantage of many polymers, however, is that, since they are polyols, they are susceptible to crosslinking at high pH by the presence of even a low concentration of multivalent cation, such as iron (III) ions.

In drilling some subterranean formations, and often particularly those bearing oil or gas, hydrogen sulphide accumulations are frequently encountered. The drilling fluid brings the hydrogen sulphide to the surface. Such sulphide in the drilling fluid is problematic, as it can

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0 corrode the steel in the drilling apparatus and may be liberated into the atmosphere as toxic sulphide gas at the well surface.

Generally, to protect the health of those working with the drilling fluid and those at the surface of the well, conditions should be maintained to ensure that the concentration of hydrogen sulphide above the fluid, emitted due to the partial pressure of the gas, is less than about 15 ppm. The partial pressure of hydrogen sulphide at ambient temperature is a function of the concentration of sulphide ions in the fluid and the pH of the fluid. To ensure that the limit of 15 ppm is not exceeded even for the maximum sulphide concentration that may be encountered in a subterranean formation, the pH of the drilling fluid is typically maintained at a minimum of about 11.5. Also, to prevent the soluble sulphide concentration in the fluid from becoming excessive, action is routinely taken to remove sulphide from the fluid.

A common process for removing sulphide from drilling fluids is by precipitation, usually with a solid zinc compound. Zinc compounds commonly used are zinc oxide and zinc carbonate. These compounds react with hydrogen sulphide to form insoluble zinc sulphide. In insoluble form, the sulphide is relatively harmless (unless the pH falls to acid conditions) and can be removed from the fluid by known separation techniques.

Because these zinc compounds are solids, the reaction rate can be slow, which is especially undesirable when high concentrations of sulphide are encountered or when removal of final traces of sulphide is desired. However, soluble zinc salts can not be used as they hydrolyze at low pH, forming gelatinous hydroxide. While the gelatinous hydroxide would still react with the sulphide, the gelatinous solid would likely interfere with the rheological properties of the drilling fluid. Also, zinc salts behave as acids and tend to reduce the pH of the fluid, increasing the risk of greater emission of hydrogen sulphide into the air..

U.S. Patent No. 4,242,655 to Carney discloses a soluble form of zinc in a chelated form for use as a hydrogen sulfide scavenger in an oil well. The chelating agents disclosed in U.S. Patent No. 4,242,655 are low molecular weight hydrocarbon based materials containing acetic or nitrogen functional groups with a stability constant in the range of about 10-16, as described by Chaber Martell in Organic Sequestering Agents. Zinc chelates with a stabilizing constant outside of this range of about 10-16 are said to be either ineffective for removing soluble sulphide ion or to adversely affect the rheology of the well fluid.

Various zinc compounds--both soluble and insoluble--have been used as sulphide scavengers for many years and are generally regarded as an industry standard. However, all zinc compounds have the disadvantage that zinc is regarded as a toxic heavy metal whose discharge

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0 must be carefully controlled to protect the environment. When a zinc scavenger is used in the drilling fluid, the cuttings, as well as the residual fluid at the end of the drilling operation, will be contaminated with zinc. Environmental awareness is growing worldwide and discharge of waste containing zinc into the sea or uncontrolled land fill sites is becoming increasingly unacceptable. However, if all zinc contaminated waste from drilling activities had to be directed to special waste
5 disposal sites, many commercial operations would be unviable.

Most other heavy metals which react with hydrogen sulphide to form insoluble sulphide such as copper (both oxidation states), mercury, lead, and nickel, also cause environmental concerns and thus are no more acceptable than zinc.

An exception is iron, a metal, that also forms insoluble sulphide upon reaction with
10 hydrogen sulphide but which is largely free from environmental concerns. Iron salts, however, have been found to be unsuitable as sulphide scavengers because the compounds are not stable in solutions at high pH. At the pH used in drilling fluids, both iron (II) and iron (III) are precipitated as gelatinous iron hydroxide, which would have unacceptable effects on the rheology of the drilling fluid.

15 Solid Fe_3O_4 has sometimes been added to drilling fluids in the same way as basic zinc carbonate, but the reaction of the iron oxide is slower than zinc carbonate, particularly at the high pH required for drilling fluids exposed to hydrogen sulphide. The reason for the slower action of the iron compound compared to that of zinc is not fully understood. However, currently available sulphide scavengers based on iron are widely recognized as less efficient and less effective
20 scavengers than scavengers based on zinc. Consequently, the environmentally attractive option has been the less effective option.

U.S. Patent No. 4,756,836 to Jeffrey et al. teaches using an iron chelate as a downhole hydrogen sulphide scavenger in drilling mud, particularly water based clay muds. This patent discloses chelates of iron with hydroxylethylenediaminetriacetic acid (HEDTA), nitrilotriacetic
25 acid (NTA), ethylenediaminetetraacetic acid (EDTA), and diethylenetriaminepentaacetic acid (DTPA). The chelates are said to convert hydrogen sulphide to sulphur. Claimed advantages of this invention are said to be that the iron chelate is regenerated by oxygen at the surface and that the iron scavenges oxygen in the mud stream to cut down oxygen assisted corrosion of the drill stem. This patent further teaches that whether the iron is supplied in the Fe (II) or Fe(III) form,
30 exposure to oxygen at some point in the mud flow changes the form to Fe (III) to prepare the chelate for hydrogen sulphide conversion. Oxygen exposure in an aerated mud pit or in the shale shaker or by another oxygen source is said to aid regeneration of the iron chelate.

0 While iron (III) is known to readily chelate with EDTA, NTA and HEDTA and DTPA, such complexes have limited stability at high pH. Iron in these complexes is well known to tend to precipitate out as ferric hydroxide at a pH greater than 9. For example, manufacturers of these chelates typically quote stability or effectiveness as an Fe(III) chelate, of NTA at pH 1-3, DPTA at pH 1-7, EDTA at pH 1-6, and HEDTA at pH 1-9. At pH higher than such ranges, these
5 chelating agents lack ability to stabilize the iron against precipitation as the hydroxide. For effective use as a scavenger according to the teachings of Jeffrey invention of U.S. Patent No. 4,756,836, the iron must stay in chelated form. Further, the multivalent nature of iron III is likely to cause crosslinking of polymers in a polymer based drilling mud, leading to gelation and interference with the rheology of the fluid.

10 A continuing need exists for environmentally friendly hydrogen sulfide scavengers suitable and effective for use in polymer based drilling fluids.

Summary of the Invention

15 The present invention provides an environmentally friendly method of removing hydrogen sulphide or sulphide ions from fluids having a pH in excess of about 9 and even ranging as high as about 11 to 12 or higher. In the method, iron chelating agents having stability at such high pH, particularly ferrous gluconates, are added to the fluid in quantities sufficient to form iron sulphide with the sulphide ion. Stronger chelation of iron may be realized by adding an excess of the gluconate group than the stoichiometric equation would suggest would be required for the chelation. The iron chelating agent is mixed with the fluid and an iron sulphide precipitate is
20 formed. The hydrogen sulphide or sulphide ion concentration in the fluid may be maintained at or below a desired level by maintaining the iron chelating agent content of the fluid at a certain effective level.

25 This method is particularly suited for removing hydrogen sulphide from a drilling fluid used in drilling a well or borehole in a hydrocarbon bearing formation where hydrogen sulphide is frequently encountered. The pH of such drilling fluids is commonly maintained at about 11.5 to keep the hydrogen sulphide in solution in the fluid and to avoid hydrogen sulphide emission into the air at the surface of the well.

30 The present invention further comprises an additive for drilling fluids comprising iron chelating agents having stability at a pH in excess of about 9 and most preferably in excess of about 11. The additive comprises ferrous gluconate in an effective amount for removing hydrogen sulphide from said fluid.

Description of the Preferred Embodiment

In the past, the limited stability of known iron chelating agents such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid (HEDTA) and diethylenetriaminepentaacetic acid (DTPA), limited their utility as sulphide scavengers for high pH drilling fluids typically used in drilling wells in subterranean formations. The sulphide scavenger mechanism suggested by U.S. Patent 4,242,655 to Carney--that the metal complex needs to be strong enough to confer stability in a solution of high pH, i.e., so that the metal is not precipitated as the hydroxide, but conversely the solubility of the sulphide needs to be sufficiently low so as to allow the metal to be removed from the chelated form and precipitated as the sulphide-- has further cast doubt on the utility of iron compounds as a sulphide scavenger in drilling fluids. That is, the solubility product of iron II hydroxide is 8.0×10^{-16} whereas the solubility product of iron sulphide is 8.0×10^{-18} , values differing by only a relatively small factor of 100. Generally, the solubility products of metal salts such as sulphides and hydroxides are a guide to the solubility of the salts. Hence, the small difference in solubility product between iron sulphide and iron hydroxide has indicated that iron chelating agents may have very limited utility as sulphide scavengers.

Efforts to locate an iron chelating agent for use as a sulphide scavenger at high pH applying the teaching of U.S. Patent No. 4,756,836 to Jeffrey et al. have resulted in tests of ethylenediaminebis(2-hydroxyphenylacetic acid)(EDDHA) and similar multidentate ligands. The tests have indicated that EDDHA and EDDHA type compounds show stability as iron chelating agents at pH 11, but tend to form gels in drilling fluids. Such gels are believed to result from crosslinking of the polymers in the fluids caused by the trivalent iron ions in these compounds. Gels in drilling fluids are likely to cause rheological problems, making the fluid difficult to pump, and efforts to pump the fluid could lead to fracturing the well.

Specifically, test of Fe(III) EDDHA complex in a polymer-based fluid showed the following observations: at pH 11.5, a brown ferric hydroxide precipitate and hence lack of stability as a chelating agent; at pH 11.0, no precipitate, but stringy mud becoming gelatinous on standing; and at pH 10.5, again stringy mud that gelled on standing. The formulation of this drilling fluid was: 0.75 oil free barrel (bbl) saturated sodium chloride solution; 1.0 pound (avoirdupois) per barrel (ppb) carboxymethyl cellulose; 1.5 ppb starch; 1.0 ppb xanthan gum; 3.0 ppb sodium polyacrylate; and 1.5 ppb potassium hydroxide.

Phosphonates have also been considered as potential ligands for the formulation of iron based sulphide scavenger, but these have some potential disadvantages. Phosphonates are

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0 generally slightly toxic, poorly biodegradable and tend to be effective dispersants--all three are unattractive features for a compound to be used in a drilling fluid.

Nevertheless, because of the bio-friendly nature of iron, efforts have continued to find useful iron chelating agent for sulphide scavenging in drilling fluids.

5 The present invention provides methods for scavenging sulphide in high pH fluids that are particularly suitable for drilling fluids used in drilling wells in hydrocarbon-bearing subterranean formations. The methods employ an additive comprising an organic compound from a group capable of acting as a chelating agent with iron. The iron chelate compounds or complexes are stable at high pH and do not form gels in polymer based fluids, making the complexes or compounds excellent sulphide scavengers for use in drilling fluids. Particularly, gluconic acid has
10 been found to form stable complexes with iron (II) at pH above 9 and even at pH ranging from about 11 to 12 or higher, the pH most commonly desired for drilling fluids that are in contact with soluble sulphide or hydrogen sulphide.

Iron(II) or ferrous gluconate is commonly used as an iron supplement for dietary purposes and thus is considered non-toxic. Further, the gluconic moiety is derived from glucose and thus
15 iron (II) gluconate is also fully biodegradable. Heptagluconate may be substituted for gluconate in the compounds or complexes of this invention and the term "gluconate" as used herein shall be understood to encompass "heptagluconate" as well.

Iron (II) gluconate as a sulphide scavenger has an advantage of being a readily available and environmentally friendly or environmentally acceptable compound or complex. Moreover,
20 iron(II) gluconate is effective as a sulphide scavenger. It also does not impair the properties of the drilling fluid to which it is added.

In the method of this invention, ferrous gluconate or an additive comprising ferrous gluconate is added to the drilling fluid. This additive may typically be added to the fluid in the mud pit, before the fluid has circulated or before the fluid contains any detectable amount of
25 sulphur or hydrogen sulphide, as a prophylactic measure against any hydrogen sulphide the fluid may encounter downhole. However, alternatively or additionally, the additive may be added after the fluid has been circulating downhole and has already encountered sulphur or hydrogen sulphide and contains same.

The ferrous or iron gluconate may be added in solid or liquid form. If in liquid form, the
30 preferred carrier fluid is water. Any other components of the additive should not be of the type that can interfere with the chelating action of the gluconate with the iron or with the stability of the complex. Further, any such other components should preferably not be of a type to cause

0 crosslinking of polymers, particularly if the fluid is polymer based. The quantity of ferrous gluconate to be added will generally depend on the quantity of hydrogen sulphide desired to be removed or scavenged. Generally, one mole of ferrous gluconate will remove one mole of hydrogen sulphide. Stronger chelation of the iron may result when an excess of the gluconate is present in the fluid for the amount of hydrogen sulphide in the fluid.

5 To test the efficacy of this invention, particularly for use of the invention in high pH drilling fluids used in drilling wells in hydrocarbon-bearing subterranean formations, a series of experiments were conducted. These tests are described below.

Experiments

EXAMPLES 1 AND 2

10 These tests were conducted to show the effect of adding iron(II)gluconate to a drilling fluid having a composition typical for that which would be used in drilling a well in a subterranean formation thought to contain hydrogen sulphide. Example 1 served as a control, with no iron(II) or other sulphide scavenger added to the drilling fluid. Example 2 involved adding 2ppb ferrous gluconate to the drilling fluid, simulating an amount that might be added as a prophylactic measure
15 against possible future influx of hydrogen sulphide in the formation. In these tests, the drilling fluid did not contain hydrogen sulphide or sulphide ions.

Details of the tests and the results, showing mud properties of the drilling fluid, are set forth in TABLE I.

TABLE I

FORMULATION	EXAMPLE 1		EXAMPLE 2	
Saturated NaCl brine	0.751 bbl*		0.751 bbl*	
Carboxymethyl cellulose	1.0 ppb**		1.0 ppb**	
Starch	1.0 ppb		1.5 ppb	
Xanthan	1.0 ppb		1.0 ppb	
Thinner	3.0 ppb		3.0 ppb	
KOH	1.5 ppb			
Barite	338.0 ppb		338.0 ppb	
FE gluconate	-		2 ppb	
	FRESH	16 HRS, 260°F	FRESH	16 HRS, 260°F
600/300***	135/97	44/28	68/45	85/55
200/100***	82/56	19/12	31/21	42/30
6/3***	15/12	3/2	6/5	8/6
PV(cps)	38	16	23	30
YP(lb/100 ft ²)	59	12	22	25
10 sec gel (lb/100 ft ²)	15	2	7	6
10 min gel (lb/100 ft ²)	32	4	16	9
API Fluid Loss (ml)		4.2 ml		3.2 ml
HTHP Fluid Loss (ml)		10.4 ml		9.6 ml
pH	11.85	10.4	11.1	9.9

* bbl = oil field barrel (159liters)

** ppb = concentration in pounds (avoirdupois) per barrel

*** Rheometer data, i.e., the figures in the first or left hand column give the speed of rotation of the rheometer bob (rpm); the figures in the other columns are the rheometer deflection

The drilling fluids were assessed in a fresh condition and again after being enclosed in a metal cell and rolled in an oven at a temperature at 260 degrees Fahrenheit for 16 hours, to simulate the treatment of the drilling fluid in field conditions. As known to those skilled in the art, hot rolling at such temperatures used in these examples often causes some degradation of the polymers and a decrease in the viscosity of the drilling fluid. The tests results in TABLE I show that the untreated drilling fluid--Example 1--had higher rheology when fresh. However, the test

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0 results for Example 2 show that ferrous gluconate had the ability to stabilize the properties of the fluid against the thinning effect of high temperature ageing.

The filtration properties of drilling fluids are commonly measured by their ability to block filter papers as set forth in the standard API Fluid Loss Test and the HTHP Fluid Loss Test, standard tests well known to those in the oil industry. The numerical results of these tests in
5 Example 1 and Example 2 are shown in TABLE I. These results represent the filtrate passing through the filter paper under standard conditions of temperature and pressure. Comparing the results of Example 1 and Example 2 shows that addition of ferrous gluconate to the drilling fluid in Example 2 was not detrimental to the filtration properties of the fluid.

10 The results shown in TABLE I for Examples 1 and 2 show that adding iron(II) or ferrous gluconate to drilling fluids does not impair the properties of the drilling fluids.

EXAMPLES 3, 4, AND 5

Tests were conducted to show the effect of adding iron(II)gluconate to a drilling fluid already contaminated with hydrogen sulphide. In preparing the fluid samples for testing, a quantity (1.5 grams) of sodium sulphide (Na_2S) was added to each sample of drilling fluid. The
15 samples were then hot rolled and allowed to cool before any sulphide scavenger was added to Examples 4 and 5. Example 3 remained without any sulphide scavenger to serve as a control. After cooling, iron(II) gluconate was added as a sulphide scavenger to Examples 4 and 5 and all of the fluids were hot rolled again. In Example 4, iron(II) gluconate was added in solid form, and in Example 5, iron(II) gluconate was added in liquid form, to examine whether the physical form
20 of the scavenger had any effect on its performance. Details of the tests and the results, showing mud properties of the drilling fluid, are set forth in TABLE II.

TABLE II

FORMULATION	EXAMPLE 3		EXAMPLE 4		EXAMPLE 5	
Saturated NaCl brine	0.751 bbl*		0.751 bbl*		0.751 bbl*	
Carboxymethyl cellulose	1.0 ppb**		1.0 ppb**		1.0 bbp**	
Starch	1.5 ppb		1.5 ppb		1.5 ppb	
Xanthan	1.0 ppb		1.0 ppb		1.0 ppb	
Thinner	3.0 ppb		3.0 ppb		3.0 ppb	
KOH	1.5 ppb		1.5 ppb		1.5 ppb	
Barite	338.0 ppb		338.0 ppb		338.0 ppb	
Na ₂ S	1.5 ppb		1.5 ppb		1.5 ppb	
Fe gluconate	-		2.0 ppb (solid)		2.0 ppb (in solution)	
	Fresh	16 hrs; 260°F	Fresh	16 hrs; 260°F	Fresh	16 hrs; 260°F
600/300***	68/40	27/15	41/24	30/19	34/19	30/19
200/100***	28/17	10/8	17/12	12/9	13/8	12/9
6/3***	3/2	4/3	3/2	2/1	2/1	2/1
PV (cps)	28	12	17	11	15	11
YP (lb/100ft ²)	12	3	7	8	4	8
10 sec gel (lb/100ft ²)	2	3	2	1	1	1
10 min gel (lb/100ft ²)	6	5	4	3	3	3
API Fluid loss (ml)		N/D		3.6 ml		3.8 ml
HTHP (ml)		N/D		13.8 ml		12.8 ml
pH	12.4	11.1	12.3	11.6	12.3	11.6

* bbl = oil field barrel (159liters)

** ppb = concentration in pounds (avoirdupois) per barrel

*** Rheometer data, i.e., the figures in the first or left hand column give the speed of rotation of the rheometer bob (rpm); the figures in the other columns are the rheometer deflection

The results in TABLE II show that iron(II) gluconate behaves the same whether in liquid or solid form--one form does not appear to perform significantly better than the other as a sulphide scavenger in drilling fluids. All of the drilling fluids tested in these Examples 3, 4 and 5 showed significant degradation of rheological properties, probably because all had been hot rolled for a

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0 total of 32 hours. However, the untreated fluid, i.e., the fluid without the iron(II) gluconate additive,--Example 3--showed more degradation than the fluids with the iron(II) gluconate additive--Examples 4 and 5.

Like the results in TABLE I, the results in TABLE II indicate that adding iron(II) or ferrous gluconate to drilling fluids does not impair the properties of the drilling fluids.

5 EXAMPLES 6, 7, AND 8

In Examples 3, 4, and 5 discussed above, the samples were pretreated with 1.5 ppb sodium sulphide. However, in field conditions, the drilling fluid may be exposed to a higher concentration of sulphide or hydrogen sulphide before the iron(II) gluconate scavenger is introduced into the drilling fluid. This circumstance would lead to a higher loading of iron sulphide in the drilling fluid. To test whether such higher loading could lead to detrimental effects, drilling fluid samples--Examples 6, 7, and 8--were prepared with a concentration of 2.8 ppb sodium sulphide (or about twice the concentration used in Examples 3, 4 and 5). Solid or liquid iron(II) gluconate was added to Examples 7 and 8, while Example 6 served as a control, and the fluids were hot rolled for 16 hours.

15 Details of the tests and the results, showing mud properties of the drilling fluid, are set forth in TABLE III.

TABLE III

FORMULATION	EXAMPLE 6		EXAMPLE 7		EXAMPLE 8	
Saturated NaCl brine	0.751 bbl*		0.751 bbl*		0.751 bbl*	
Carboxymethyl cellulose	1.0 ppb**		1.0 ppb**		1.0 ppb**	
Starch	1.5 ppb		1.5 ppb		1.5 ppb	
Xanthan	1.0 ppb		1.0 ppb		1.0 ppb	
Thinner	3.0 ppb		3.0 ppb		3.0 ppb	
KOH	1.5 ppb		1.5 ppb		1.5 ppb	
Barite	338.0 ppb		338.0 ppb		338.0 ppb	
Na ₂ S	2.8 ppb		2.8 ppb		2.8 ppb	
Fe gluconate	-		2.0 ppb (solid)		2.0 ppb (in solution)	
	Fresh	16 hrs; 260°F	Fresh	16 hrs; 260°F	Fresh	16 hrs; 260°F
600/300***		25/15	47/29	55/35	60/40	55/35
200/100***		10/7	20/12	28/18	30/10	28/19
6/3***		3/2	3/2	5/4	5/4	5/4
PV (cps)		10	18	20	20	20
YP (lb/100ft ²)		5	11	15	20	15
10 sec gel (lb/100ft ²)		3	2	6	6	6
10 min gel (lb/100ft ²)		7	4	13	10	11
API Fluid loss (ml)		N/D		4.6 ml		5.6 ml
HTHP (ml)		N/D		12.0 ml		14.0 ml
pH	12.4	N/D	12.3	11.3	12.3	11.3

* bbl = oil field barrel (159liters)

** ppb = concentration in pounds (avoirdupois) per barrel

*** Rheometer data, i.e., the figures in the first or left hand column give the speed of rotation of the rheometer bob (rpm); the figures in the other columns are the rheometer deflection

The results shown in TABLE III are similar to the results shown in TABLES I and II. That is, adding iron(II) or ferrous gluconate to drilling fluids does not impair the properties of the drilling fluids. Also, the iron(II) or ferrous gluconate additive is equally effective as a sulphide scavenger in solid or liquid form.

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0 EXAMPLES 9, 10 and 11

 Tests were conducted to show the effect of adding hydrogen sulfide to a drilling fluid already treated with iron(II)gluconate scavenger. In preparing the fluid samples for testing, a quantity (2.8 grams) of sodium sulphide (Na_2S) was added to each sample of drilling fluid. The samples were then hot rolled, after which iron(II) gluconate was added as a sulphide scavenger and
5 the fluids were hot rolled again.

 Details of the tests and the results, showing mud properties of the drilling fluid, are set forth in TABLE IV.

TABLE IV

FORMULATION	EXAMPLE 9		EXAMPLE 10		EXAMPLE 11	
Saturated NaCl brine	0.751 bbl*		0.751 bbl*		0.751 bbl*	
Carboxymethyl cellulose	1.0 ppb**		1.0 ppb**		1.0 bbp**	
Starch	1.5 ppb		1.5 ppb		1.5 ppb	
Xanthan	1.0 ppb		1.0 ppb		1.0 ppb	
Thinner	3.0 ppb		3.0 ppb		3.0 ppb	
KOH	1.5 ppb		1.5 ppb		1.5 ppb	
Barite	338.0 ppb		338.0 ppb		338.0 ppb	
Fe gluconate	2.0 ppb		2.0 ppb		2.0 ppb	
Na gluconate	1.0 ppb		2.0 ppb		-	
Na ₂ S	2.8 ppb		2.8 ppb		2.8 ppb	
	Fresh	16 hrs; 260°F	Fresh	16 hrs; 260°F	Fresh	16 hrs; 260°F
600/300***	49/26	34/20	59/30	38/23	48/31	29/19
200/100***	18/10	14/9	20/12	16/10	22/13	12/8
6/3***	2/1	6/2	2/1	3/2	4/2	3/2
PV (cps)	23	14	29	15	17	10
YP (lb/100ft ²)	3	6	1	8	14	9
10 sec gel (lb/100ft ²)	2	3	2	3	3	3
10 min gel (lb/100ft ²)	12	10	4	10	7	7
API Fluid loss (ml)	-	5.4	-	5.2	-	6.0
HTHP (ml)	-	13.0	-	12.6	-	13.6
pH	11.6	11.4	11.58	11.3	11.65	11.3

* bbl = oil field barrel (159liters)

** ppb = concentration in pounds (avoirdupois) per barrel

*** Rheometer data, i.e., the figures in the first or left hand column give the speed of rotation of the rheometer bob (rpm); the figures in the other columns are the rheometer deflection

The results shown in TABLE IV are similar to the results shown in the other tables discussed above.

EXAMPLES 12, 13, 14, 15, AND 16

An important property of iron(II) gluconate is that it reacts quantitatively with sulphide in solution. The sulphide content of filtrate from the Examples discussed in TABLES II - IV above, however, cannot accurately show this property, however, because barite, present in all of these examples, has some slight ability to scavenge sulphide ions, probably due to the small zinc content in barite. To show this property of iron(II) gluconate, a series of specially formulated fluids was made up with the aim of measuring the stoichiometry of the sulphide/iron(II) gluconate reaction. Each test series omitted any constituent or component that might interfere with accurate analytical determination of sulphide in the treated fluid.

In the method for these tests, sodium chloride brine (1.2 sg) was treated with potassium hydroxide to bring the pH of the fluid to about 11.5 or 12 for each Example. Iron(II) gluconate was added to Examples 14, 15, and 16 but not to Examples 12 or 13. Examples 12 and 13 served as controls to access the initial concentration of sulphide. The fluids were well mixed and sodium sulphide (1.1g or 2.5 g) was added to each Example before rolling at 150 degrees Fahrenheit for two hours. Examples 12 and 13 were filtered and the filtrate was analyzed for sulphide. For each Example 12 - 16, an experimentally determined concentration of the sulphide was recorded along with the expected sulphide concentration. The expected final concentration of sulphide was calculated on the basis of the amount of iron and sulphide added to the reaction mixture, incorporating the assumption that the reaction was quantitative.

Details of the tests and the results are set forth in TABLE V.

TABLE V

EXAMPLE	CHELATE USED	MOLES OF S ⁻ ADDED (mole/350 ml)	SULPHIDE DETERMINED IN FILTRATE (S ⁻ mg/l)	MOLES OF METAL SCAVENGER per 350 ml	PREDICTED SULPHIDE IN FILTRATE (mg/l)
12	No chelate	0.0034	300	-	300
13	No chelate	0.0074	700	-	700
14	2.0g Fe gluconate	0.0034	0	0.0048	0
15	3.0g Fe gluconate	0.007	200	0.0048	200
16	2.0g Fe gluconate + 1.0g Na gluconate	0.0075	200	0.0048	200

0

The results in TABLE V show that the reaction between iron(II) gluconate and sulphide is quantitative. When the iron(II) gluconate additive was present in molar excess, the residual sulphide concentration was zero, indicating that this iron chelate can precipitate all of the sulphide in solution. Furthermore, the reaction was complete within two hours of contact time. This rapid reaction is probably due to ionic interaction between the iron and sulphide. However, for whatever reason, this rapid reaction indicates that iron(II) gluconate can be an effective scavenger of sulphide ions in drilling fluids.

5

10

Further, considering the results shown in TABLES I-IV, use of ferrous or iron(II) gluconate as a sulphide scavenger in drilling fluids is not detrimental to the rheology of the fluid or to the fluid loss performance of the fluid. The fluids containing the scavenger surprisingly yielded even better rheological results than fluids hot rolled with sulphide only. That is, not only does iron(II) gluconate not detract from desirable properties of drilling fluid, but iron(II) gluconate improves those properties.

15

The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described composition and method can be made without departing from the intended scope of this invention as defined by the appended claims.

1 I claim:

1 1. A method of removing sulphide ion from a fluid having a pH in excess of about 9
2 comprising:

3 adding a ferrous gluconate chelating agent to said fluid in sufficient quantity to form iron
4 sulphide with the sulphide ion; and

mixing the chelate with the fluid and forming iron sulphide.

1 2. The method of claim 1 further comprising maintaining the ferrous gluconate at a level to
maintain the sulphide concentration below a certain desired level.

1 3. The method of claim 1 wherein the quantity of gluconate added to said fluid exceeds the
2 quantity needed to chelate all of the iron in said fluid.

1 4. A method of reducing the hydrogen sulphide concentration in a drilling fluid comprising:

2 adding a ferrous gluconate compound to said fluid; and

3 allowing said ferrous gluconate to react with said hydrogen sulphide such that sulphide
4 is precipitated.

1 5. The method of claim 4 wherein said sulphide is precipitated as iron sulphide.

1 6. The method of claim 4 wherein said drilling fluid has a pH greater than 9.0.

1 7. The method of claim 4 wherein said drilling fluid has a pH ranging from about 11 to
2 about 12.

1 8. A drilling fluid additive comprising an iron (II) based hydrogen sulphide scavenger
2 chelated with a gluconate chelating agent which provides a stable complex with said iron at pH
3 greater than about 9.

- 1 9. The drilling fluid additive of claim 8 which provides a stable complex with said iron at a
2 pH of at least about 11.5.
- 1 10. The drilling fluid additive of claim 8 which provides said stability at subterranean
2 formation temperatures.
- 1 11. The drilling fluid additive of claim 8 which provides said stability at temperatures ranging
from ambient temperature to over 300 degrees Fahrenheit.
- 1 12. The drilling fluid additive of claim 8 which provides improved resilience to the rheological
properties of said fluid.
- 1 13. In combination with a drilling mud comprising crosslinkable polymers delivered to a well
2 during drilling operations, an additive for decreasing hydrogen sulphide concentration in the mud,
3 the additive comprising an effective amount of a ferrous chelating agent mixed into the mud to
4 reduce hydrogen sulphide concentration in the mud circulating in the well, wherein such additive
5 fails to significantly cause crosslinking of said polymers.
- 1 14. The additive of claim 13 wherein the iron in said ferrous chelating agent does not
significantly ionize to a trivalent state in said mud.
- 1 15. The additive of claim 13 wherein said additive enhances the mud's ability to withstand
well temperatures under shear.
- 1 16. A polymer based drilling fluid comprising ferrous gluconate.

ABSTRACT

An environmentally friendly method and composition is provided for removing hydrogen sulphide from fluids at high pH. The method and composition are particularly suited for removing hydrogen sulphide from drilling fluids used in drilling boreholes in hydrocarbon bearing subterranean formations, and are suitable for use with any drilling fluid, including polymer based drilling fluids. The sulphide scavenger used in the method and composition is a ferrous gluconate, an organic iron chelating agent stable at pH as high as 11.5, the pH preferred for drilling fluids that may encounter hydrogen sulphide. Further, this additive has been found to enhance the resilience of the rheological properties of drilling fluids to hot rolling and comparable field conditions.

10